Description

Microstructured Gas Sensor with Gas-Sensitive Properties Controlled by Imposition of an Electric Field

The invention relates to a microstructured gas sensor according to the features of the preamble of Claim 1.

Such microstructured gas sensors are disclosed for example in DE 44 42 396 A1 and DE 195 44 303 A1.

In recent years, resistive gas sensors have been increasingly used to measure air pollutant concentrations in the ppm and ppb range. The main advantage of such semiconductor gas sensors is their low manufacturing cost combined with the simplicity of hybrid integration into electronics for the conditioning of measurements. Semiconductor gas sensors are electrical conductance sensors. At operating temperatures of 50 °C to 900 °C the electric resistance of the semiconductor film changes upon contact with the gas for detection. This reversible reaction makes possible the electronic detection of a gas. Typical detected gases are NO_x, CO, hydrocarbons, NH_3, O_3, and H_2O. Both the electrode structures and the gas-sensitive films of these sensors are fashioned chiefly by thick-film and thin-film methods. Common materials for the active sensing elements are semiconducting metal oxides such as[1] SnO_2, WO_3, In_2O_3, Ga_2O_3 $Cr_{2-x}Ti_xO_3$, etc., and organic semiconductors (polypyrrole, polyaniline, and phthalocyanine) [1]. Here the temperature is usually employed to control the chemical reaction on the semiconducting films.

In these arrangements, heaters and temperature sensor structures are usually integrated on a suitable substrate platform. The sensitive metal oxide films such as for example SnO_2 are then deposited on such platforms by thick-film and thin-film methods. Concentration of heat development by the heater is concentrated on the sensitive surface with the aid of microstructured

[1] A comma was probably intended after Ga_2O_3.—Translator.

substrate platforms, while the surrounding region can remain cold. This is advantageous for example in order to locate the detection electronics on the cold part of the substrate [2]. Thermal decoupling is effected for example with thin membranes of SiO_2/Si_3N_4 or so-called hotplate structures [3].

Semiconductor gas sensors (metal oxide sensors) are based on the (simplified) functional principle that gas molecules are adsorbed at semiconductor surfaces and a certain portion of them enter into a chemical bond with the semiconductor (chemisorption). Electrons are localized/bound in the semiconductor-adsorbate complex or liberated by it. In the band model of the semiconductor, this corresponds to occupation of a surface state (with electrons or holes) that must, in terms of its energetic position, be localized near the Fermi energy in the band gap [4].

Because the bound charge carriers are no longer available for current transport, this reoccupation of surface states is usually detected with conductance sensors. An approximately equivalent option for measurement, so far not utilized in industry, comprises surface potential sensors (e.g., SGFET) [5, 6]. The central disadvantage of the known arrangements (e.g., SGFET) is that no design takes into account the planar manufacturing methods of conventional semiconductor fabrication.

The reoccupation of surface states results in a shift in the energy levels (position of the Fermi level). This in turn has retroactive effects on the surface states themselves, because the energy levels available are now differently distributed. This is why, for example, only a portion of the adsorbed gas molecules can go over to the chemisorbed state, because the occupation probability of the surface state is diminished along with the position of the Fermi level under chemisorption (self-blocking, "Weisz effect") [7].

What is more, from the principles of semiconductor electronics it is known that the position of the Fermi level can be affected not just by the temperature and doping but also by electric fields. In gas sensors of the prior art, the position of the Fermi level is determined through the temperature; in the present invention it is determined through electric fields. This is also known as "electroadsorption." If, therefore, an electric field is impressed on a gas-sensitive semiconductor surface, the shift in the Fermi level brought about in this way makes it possible to control the adsorption probability (chemisorption and physisorption) of gases on these surfaces. Gas sensors can therefore be made subject to electrical modulation of their sensitivity to various gases. In this way a parameter for gas sensors, adjustable with no power consumption, becomes available such that the sensitivity modulation can be substantially expanded in terms of response time and selectivity through the heater temperature.

This electroadsorptive effect was postulated by Fedor Wolkenstein in 1957 [8]. Because it requires very high electric fields (close to the dielectric breakdown strength of air), however, it was not until 1968 that Hoenig and Lane, after great experimental effort, experimentally confirmed the occurrence of the effect on a zinc oxide film placed in a flat-plate capacitor [9].

The potential inherent in this electrical sensitivity control of MST[2] gas sensors was immediately recognized by these groups [10, 11, 12] and manifested itself in a rather large number of patent applications for such sensors; up to now, however, no gas sensor has been developed whose design is oriented to the vertical electrical controllability of its sensitivity.

The invention pursues the goal of an improved gas sensing technology through the use of the electroadsorptive effect with small and low-cost sensors that can find use in, among other fields, production and process metrology, automobile manufacture, safety engineering, and climatic and

[2] Presumably *Mikrosystemtechnik,* hence = microsystems technology; but it is possible *Mikrostrukturiert* (= microstructured, micromachined) was meant.—Translator.

environmental monitoring. The invention makes it possible to implement semiconductor gas sensors with markedly better properties than heretofore. In particular, the gas sensor according to the invention is to have enhanced selectivity and becapable of functioning at lower operating temperatures, that is, significantly below 300 °C.

This goal is achieved with a microstructured gas sensor having the features of Claim 1.

Developments of this gas sensor are identified in the dependent claims.

The invention is based on gas sensors functioning on the basis of gas-sensitive semiconductor materials. In contrast to known gas sensors made of semiconductor material, in which a change in resistance in the resistor film is read out solely by two electrodes, in the sensors according to the invention there are additionally at least one, but advantageously a plurality of electrodes inside the semiconductor body of the gas sensor for controlling the selectivity. This (these) further electrode(s) is (are) located under the resistor film and are isolated from it by an insulator film. This (these) further electrode(s) serves (serve) to produce an electric field acting on the semiconductor. The effect of electric fields on the gas reaction of the sensitive film is utilized here. To this end it is necessary that an electric field produced in the semiconductor body of the gas sensor via a field electrode is effective up to the surface of the gas-sensitive film that faces toward the gas. That is to say, the films lying above the gate electrode must not screen the electric field. The Debye length L_D is a measure of the shielding length in semiconductors. According to the invention, the insulator film located between the resistor film and the further electrode(s) has a maximum thickness that is at least approximately less than or approximately equal to 10 times the Debye length of the insulator material employed. The thickness is preferably chosen approximately

less than or equal to 3 times the Debye length, and the thickness is especially preferably chosen less than or equal to this Debye length.

The Debye length L_D is here defined as follows:

$$L_D = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{q^2 N}}$$

where

T is the temperature,

ε is the relative permittivity of the material,

ε_0 is the absolute permittivity,

k is the Boltzmann constant,

N is the charge-carrier concentration and

q is the elementary charge.

In the case of the frequently used gas-sensitive material SnO_2, for example, L_D is approximately 60 to 80 nm. The screening length in insulators is theoretically very great. In a real component, however, impurities or defects and interfacial states mean that the thickness of the insulator film should not exceed 300 nm, so that a sufficiently strong electric field can still be produced in the sensitive material of the gas sensor.

Preferably, a plurality of further electrodes are arranged in the semiconductor body (question: is the semiconductor body everything or not?). This fashioning, which is preferably but not necessarily employed with the above-mentioned sizing of the insulator film, makes it possible to offset/control in a wholly purposeful way the gradient in the surface potential variation due to the potential drop between the two electrodes of the resistor film.

The sensors according to the invention comprise semiconductor materials (such as for example the metal oxides[3] SnO_2, WO_3, In_2O_3, Ga_2O_3 $Cr_{2-x}Ti_xO_{3+z}$, etc., or organic

[3] A comma was probably intended after Ga_2O_3. The expression "3 + z" in the last subscript in the list is as in the original.—Translator.

semiconductors) under which one or more further electrodes, called field electrodes in what follows, are deposited, these field electrodes being isolated by an insulator film.

The arrangements according to the invention are distinguished by, among other things, the fact that they are structured on the substrates customary in microelectronics (such as silicon and silicon dioxide). What is more, it is also possible to build on other substrates customary in gas sensing technology such as Al_2O_3 (including sapphire) in its usual forms.

It is particularly expedient to employ, between the control electrode and the semiconductor, an insulator material that can withstand a high breakdown field strength and does not screen electric fields.

The following improvements and advantages in comparison with the known art can be cited with the gas sensor according to the invention:

Conventional gas sensors are operated at high temperatures of 250 °C to 900 °C (reason: to control absorption; see above). With the arrangement according to the invention, the operating temperatures can be reduced to values below 200 °C.

The arrangement according to the invention is expected to yield an improved selectivity of the sensor for a target gas through utilization of the electroadsorptive effect.

The advantages of a low operating temperature are made still more evident by the possibility of integrating CMOS processing electronics on the sensor chip.

The sensor arrangements as described above can be operated as an integrated sensor (dosimeter) through utilization of the electroadsorptive effect.

A kinetic effect can also be introduced by modulating the gate voltage. Operation with a time-varying gate voltage periodically shifts the Fermi level in the metal oxide, that is, alteration of

the electrochemical equilibrium under the effect of an external voltage on the field electrode. Periodic modulation of the gate voltage leads to an alternating variation in the resistance of the sensitive film. Through spectral analysis of this alternating variation in resistance, it appears possible to associate distinct frequency components with distinct gases and thus to achieve a gain in selectivity.

The possibility of electrical desorption of adsorbed gases, which can be driven away from the surface of the sensitive film by a strong field pulse. In this way an initial state of the sensors is restored during continuous operation (baseline zeroing).

A further possibility (as an alternative to the finger electrode structure) for bringing about the lateral distribution of the field under the sensitive film is to fashion the control electrode as a resistor, so that the potential drop along the resistor as current flows through it is parallel to the (intended) variation in surface potential of the sensitive film.

A combination of sensor temperature variation with field control is possible.

Alternative operating modes of the controllable sensor in the linear/active region of the thin-film transistor are possible.

An adaptation of the finger electrode width to the grain size of the sensitive material, with the optimum that each finger drives one grain (or a few grains) or that the spacing of finger electrodes is in the range of the Debye length of the sensitive material or, alternatively, a finger electrode width that is less than or equal to the Debye length of the sensitive material.

In what follows, the invention is explained on the basis of exemplary embodiments with reference to the drawings, in which:

Figure 1 is a schematic representation of the mode of action of a gas-sensitive sensor according to the invention;

Figure 2 depicts a first embodiment of the gas sensor with a single field electrode located in the semiconductor body;

Figure 3 depicts a second embodiment of the gas sensor with a plurality of field electrodes located in the semiconductor body; and

Figure 4 depicts a CMOS thin-film gas sensor with control electronics in a sectional view.

The main idea of the invention (see Figure 1) is the following: If one has an electrode 1 under a gas-sensitive semiconductor 3 and an insulator film 2, then the electroadsorptive effect can occur only if the thickness of the gas-sensitive semiconductor is of the order of the Debye length L_D. In this way the surface absorption of gas 4 can be controlled through the electric field. What is more, care must be taken that the insulator is low in defects because these defects substantially shorten the Debye length of insulator 5 and thus interfere with penetration of the field to the gas-sensitive film. Examples of Debye lengths for SnO_2 are for example 60-80 nm;[6] for a real insulator these are in the range below several micrometers.

Figure 2 is a sectional view of a first exemplary embodiment of the gas sensor according to the invention. There is a semiconductor substrate 1 on which a gas-sensitive film with a thickness of for example 59 nm lies. This gas-sensitive film 4 is contacted by two electrodes 5. The gas-sensitive film can be made for example of SnO_2. The Debye length of this gas-sensitive film is approximately 80 nm. Below this gas-sensitivefilm 4 there is a field electrode 2 isolated by an insulator film 3.

[6] The original has *60.80 nm*.—Translator.

This field electrode 2 is fashioned as a plate electrode and has its entire area located below gas-sensitive film 4. Insulator film 3 has a thickness of for example 200 nm; the Debye length of this film is approximately 300 nm if silicon oxide is employed as the material for insulator film 3.

A measure for the screening length in semiconductors is the already mentioned Debye length L_D:

$$L_D = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{q^2 N}} .$$

Thus, in the case of the frequently used gas-sensitive material SnO_2, the Debye length L_D is approximately 60 to 80 nm. The above-mentioned thickness of approximately 200 nm for insulator film 3 makes certain that a sufficiently strong electric field can be produced in the semiconductor via field electrode 2.

A further embodiment of the gas sensor according to the invention is depicted in Figure 3. In contrast to the gas sensor of Figure 2, there is now a plurality of microelectrodes 6 under the gas-sensitive film instead of a single field electrode.

The use of such microelectrodes spaced apart from one another has the following advantage. The gas-sensitive properties of a semiconductor film depend on the surface potential and thus the position of the Fermi level of the surface of gas-sensitive film 4 facing toward the gas. This effect is utilized in the present case for controlling the sensitivity and selectivity. In order to utilize this effect in optimal fashion, it is desirable to have a constant potential over the entire semiconductor surface of the gas-sensitive film.

If a voltage is applied to electrodes 5 in order to read out the resistance of gas-sensitive film

4 to electrodes 5, a potential drop appears between the two electrodes 5 and thus a gradient appears in the surface potential. By applying various voltages to microelectrodes 6, which are fashioned separately from one another, electrically isolated from one another and located under gas-sensitive film 4 inside semiconductor substrate 1, it is possible to compensate this gradient and thus set a constant potential on the semiconductor surface or shift the potential in desired directions.

The arrangements according to the invention have at their disposal a heater (see Figure 4) for the required working temperatures, which are above 100 °C. The chip must be heated to over 100 °C, because adsorbed water on the surface of the sensitive film will otherwise hinder the gas reaction. This resistive heater can, as depicted in Figure 4, be buried in the substrate or structured on the surface. Because the sensitivity of semiconductor gas sensors is a function of temperature, it is especially favorable if the heater can be controlled and/or regulated. To this end, it is desirable to integrate on the sensor chip a temperature sensor whose signal can be used to acquire the actual temperature.

The arrangement according to the invention appears particularly expedient for reducing the operating temperatures of conventional semiconductor gas sensors (250-900 °C) to values below 180 °C. For this reason, integration of CMOS circuits on the sensor chip is possible as a particular embodiment.

Figure 4 shows the schematic structure of a gas sensor with CMOS driver electronics according to the invention.

VI References

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